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Preparation of di-boride coatings by electrophoretic deposition in nanoparticle-containing molten inorganic salts

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ABSTRACT: Molten inorganic salts containing solid nanoparticles with a stable and uniform dispersion have attracted great attention as efficient heat transfer and storage materials^{1,2} and for catalysis for chemical reactions³⁻⁵. Electrophoretic deposition in molten inorganic salts containing nanoparticles, have not been reported in the literature, compared with the related wide investigations in aqueous and organic suspensions^{6,7}. Here we report the possibility of electrophoretic deposition of nanoparticles in high-temperature molten salts. In molten fluorides and chlorides, cell voltages of 1.2-1.5 V below the decomposition voltage of the electrolytes, were applied to perform the electrophoretic deposition of nanoparticles (e.g., TiB₂ and ZrB₂) on different cathode substrates, resulting in compact and adhesive coatings with high hardness. These findings should present opportunities to synthesize additional coatings and films via the proposed process.

KEYWORDS: electrophoretic deposition, molten inorganic salts, di-boride nanoparticles, di-boride coatings

Electrophoretic deposition (EPD) was discovered by Ruess in 1808, which has been investigated mostly in aqueous and organic solutions and widely used for synthesis of coatings and films⁸⁻¹⁰. However, the EPD of nanoparticles in molten inorganic salts has not been reported in the previous studies. In 1969 Kohn et al. prepared stable gold and silver sols in mixed nitrite melts (100-300 °C)¹¹. Nevertheless, they failed to conduct the electrophoretic plating of the gold colloids. Recently it has been reported that nanoparticles have been found to form stable colloids in molten halides and cyanides (90-300 °C)¹²⁻¹⁵. Thus, we are curious about that if an external cell voltage (below the decomposition cell voltage of the electrolytes) is applied on these systems such as molten halides, could the EPD of nanoparticles happen? Therefore, in this paper the EPD of ceramic di-boride nanoparticles in molten halides are carried out.

The EPD of TiB₂ nanoparticles was firstly explored in molten NaF-AlF₃ (61:39 mol) system at a temperature of 980 °C. TiB₂ nanoparticles (with a mean size of 50 nm) were added into this melt (with a content of 20 g/L), contained in a graphite crucible (Fig. 1a). A graphite anode and a molybdenum cathode were placed vertically, with a constant cell voltage of 1.2 V imposed between them for 1h, to perform the EPD. After the deposition was terminated, the electrophoretic plated cathode was lifted and removed from the cell (see the Methods section for experimental details).

Figure 1 **a**, Schematic of electrophoretic deposition (EPD) in molten salts. **b**, X-ray diffraction (XRD) pattern of the deposited coating on a molybdenum substrate in TiB₂ nanoparticle-containing molten NaF-AlF₃ (61:39 mol) system under a potentiostatic mode (1.2 V) at a temperature of 980 °C. **c-e**, Scanning electron microscopy (SEM) images (**c,d**) and photograph (**e**) (polished) (note the reflection of the pencil) of TiB₂ coating. **f**, Micrographs of the cross-section of TiB₂ coating. **g**, The dependence of indentation hardness and elastic modulus on the indentation depth for the TiB₂ coating.

The deposit on the molybdenum cathode was analyzed by X-ray diffraction (XRD) to be determined as a TiB₂ coating (Fig. 1b). The surface morphology of TiB₂ coating was characterized by scanning electron microscopy (SEM) (Fig. 1c),

showing a flat appearance. The coating was ground by 400# SiC sandpaper, then exhibited a similarly metallic luster (Fig.1e). The cross-section of TiB_2 coating as demonstrated in Fig. 1f, is revealing a flat, compact and adhesive layer, with a thickness of around 12 μm . Fig. 1g shows the dependence of hardness and elastic modulus of the TiB_2 coating on the indentation depth, with a maximum indentation depth of 500 nm. After ~150 nm, the hardness and modulus remain relatively unchanged with the increase of indentation depth. Hardness of ~40 GPa and elastic modulus of ~500 GPa are obtained (compared with the reported values of 25-35 GPa for hardness and 500-560 GPa for elastic modulus for TiB_2 ¹⁴). From these findings, it is concluded that the EPD of TiB_2 nanoparticles has been successfully achieved in molten fluorides, yielding a coherent TiB_2 coating with high hardness.

Figure 2 Micromorphology of quenched sample of TiB_2 nanoparticle-containing melt located in the upper part of molten fluorides with the addition of TiB_2 nanoparticles 5 h before.

In order to figure out the suspension state of added TiB_2 nanoparticles in the above melt, we analyzed the local nanoparticles-containing electrolyte. We sampled the upper part of molten NaF-AlF_3 salts with the introduction of TiB_2 nanoparticles 5 h before, cooled it down to room temperature quickly and characterized it by SEM (Fig. 2). It was found that TiB_2 nanoparticles still existed in the sampled solidified NaF-AlF_3 , which proves the stable suspension of TiB_2 in the molten fluorides for at least 5 h. Therefore, the achievement of the stable suspension in molten salts and the EPD on the cathode indicates the formation of stable and positively charged TiB_2 colloids in molten NaF-AlF_3 indirectly.

It is noted that a dense TiB_2 coating, without any inclusion of residual fluoride electrolyte, has been fabricated at only 980 $^{\circ}\text{C}$. Actually, powdery TiB_2 , with a melting point up to 3225 $^{\circ}\text{C}$, is difficult to be sintered to full density^{16,17}. For example, Rabiezhadeh et al. made attempts to sinter TiB_2 nanoparticles without sintering additives under hot press at 1700 $^{\circ}\text{C}$ for 2 h and obtained 92% of the theoretical density¹⁸. In the present paper the preparation of dense TiB_2 coating is probably due to the occurrence of electroosmotic motion of molten salts during the EPD of TiB_2 nanoparticles. As shown in Fig.1a, as TiB_2 nanoparticles migrates to the cathode, the electroosmotic flow of molten salts inside the not yet densified TiB_2 layer is driven away from it. In fact, it has been reported that during EPD in aqueous suspensions, the nanoparticles rearrangement is accelerated via the electroosmotic flow, leading to higher packing rates of nanoparticles¹⁹⁻²¹. It has also been suggested that for liquid assisted flash sintering, the existence of electroosmotic driven flow benefits the densification of sintering of nanoparticles²². In this paper, from the SEM image of the surface morphology (with higher magnification) of TiB_2 coating (Fig.1d), large nanoplates consisting of original nanoparticles were observed, which represents an intermediate state during the growth of TiB_2 nanoparticles. It seems that during the EPD, the EPDed TiB_2 nanoparticles on the surface of the cathode gather and grow up to form these large nanoplates with a thickness of 100-200 nm and a length of ~500 nm, with the assistance of electroosmotic flow. Finally, these nanoplates continuously grow up to collect each other to form the dense TiB_2 coating. Summarily, the occurrence of EPD of nanoparticles is accompanied by the existence of electroosmotic driven flow of molten salts, which probably promotes the forming of dense coating at a high temperature. These results also provide a novel and substantial addition to electrokinetic phenomena in colloid science.

In the same molten salts at 980 °C, a graphite cathode was employed to perform the electrophoretic deposition of TiB_2 nanoparticles (with a content of 70 g/L), via the similar procedures as the above description. In Fig. 3 a, the photo and micromorphology of the EPDed coating are presented. An apparent coating was observed on the graphite substrate and the surface micromorphology seemed relatively flat. Fig. 3 b,c shows the fractured cross-section and XRD result of the coating, which was proved to be a flat, compact and adhesive TiB_2 coating with a thickness of around 50 μm . Its micro-hardness was measured by a Vickers micro-hardness tester, giving an average value of 3500 $\text{HV}_{0.1}$. These results indicate that the successful electrophoretic deposition of TiB_2 nanoparticle on a graphite substrate in molten fluorides has been accomplished, which could lead to the possibility of producing wettable TiB_2 -coated carbon cathode for aluminum electrolysis²³.

Figure 3 a, SEM image and photograph (top-left inset) of the EPDed coating on a graphite substrate in TiB_2 nanoparticle-containing molten NaF-AlF_3 (61:39 mol) system under potentiostatic mode (1.2 V) for 1 h at a temperature of 980 °C. b,c, Micrograph of the cross-section (b) and XRD pattern (c) of the TiB_2 coating.

Besides molten fluorides, molten NaCl-KCl-AlCl_3 (45:45:10 mol) system at 710 °C was also applied to conduct the EPD of ZrB_2 nanoparticles (with a mean size of 50 nm), with the similar cell shown in Fig. 1a. A graphite anode and a graphite cathode were employed, with an applied cell voltage of 1.5 V for 1h. After the deposition, the coated cathode was removed, cleaned and dried (see the experimental details in Methods section).

Figure 4 **a**, SEM images and photograph (top-left inset) of deposited coating on a graphite substrate under a potentiostatic mode (1.5 V) in molten NaCl-KCl-AlCl₃ (45:45:10 mol) system at a temperature of 710 °C. **b-d**, XRD pattern (**b**) and micrographs of the fractured cross-section (**c,d**) of ZrB₂ coating. **e**, Typical transmission electron microscopy (TEM) image and its selected area electron diffraction (SAED) pattern (top-right inset) of ZrB₂ coating. **f**, Lattice-resolved high resolution TEM (HRTEM) image.

The electrophoretic plated coating, exhibiting a similarly metallic appearance (top-left inset of Fig. 4a), on the graphite substrate was characterized by SEM (Fig. 4a). It was found that the coating was made up of micro-particles, which consisted of nanoparticles as observed under higher magnification. The XRD pattern (Fig. 4b) with broad diffraction peaks proved that it was a ZrB₂ coating with possible nanocrystal feature. The fractured cross-section of the ZrB₂ layer was observed by SEM (Fig. 4c,d). It is dense and adhesive, with a thickness of approximately 2 μm, over the whole cross-section showing a nanostructure under higher magnification. Fig. 4e shows the transmission electron microscopy (TEM) image and the selected area electron diffraction (SAED) pattern (top-right inset of Fig. 4e) of the sample. SAED pattern included continuous but rather broad diffraction rings, which indicated polycrystalline microstructure with possible nanocrystal structure of the ZrB₂ coating. High resolution TEM (HRTEM) image is shown in Fig. 4f, which confirmed the presence of nanocrystallites. From the original nanoparticles to nanocrystal and compact ZrB₂ coating, the maintaining of the nanocrystal structure reveals the possibility of assembling nanoparticles by EPD in molten chlorides. In addition, the hardness and the elastic modulus of the ZrB₂ coating was assessed with a nanoindenter, giving the values of 20 GPa and 146 GPa, respectively. Therefore, the EPD of ZrB₂ nanoparticles has been successfully conducted in molten chlorides, resulting in a dense and adhesive ZrB₂ coating with a nanocrystal structure.

Compared with that in aqueous or organic solutions, EPD in high-temperature molten salts has the advantages as

follows. Firstly, the required cell voltages of 1.2-1.5 V in high-temperature molten salts are far below the values of 20-300 V generally applied in aqueous or organic solutions⁷. Secondly, EPD in high-temperature molten salts results in a dense and adhesive coating in one step. While in aqueous or organic solutions, the resulting deposits with high porosity, low density and poor adhesion generally need further drying and sintering, however, resulting in cracking, which is difficult to be dealt with^{7,24}. It is our anticipation that the EPD of nanoparticles in molten inorganic salts should become an important method for synthesis of ceramic coatings and films.

In summary, for the first time the EPD of ceramic di-boride nanoparticles has been demonstrated in molten halides, resulting in dense and adhesive coatings with high hardness. These findings could open opportunities to fabricate coatings and films by the proposed novel process. Molten inorganic salts represent a very attractive class of solvents (including halides, sulfides, nitrates and carbonates) for the stable dispersion and synthesis of nanomaterials (e.g., borides, oxides, carbides and nitrides)²⁵⁻²⁷. It may be assumed that the EPD can be applied to a wider range of nanoparticles and in other molten salts systems, possibly resulting in preparing more types of coatings and films with desired properties. Furthermore, if the EPD is employed for in-situ synthetic nanoparticles in molten inorganic salts, it is likely to result in additional new phenomena.

Note

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Methods

Nanoparticle-containing solid salts preparation. Two types of solid salts (i.e., fluorides and chlorides) were employed in this paper. The processes for manufacturing mixtures of solid salts and nanoparticles are the same, with the schematic shown in Fig. 5. The mixed solid NaF (>99%, Aladdin) and AlF_3 (>98%, Guanfu) or NaCl (>99%, Sinopharm) and KCl (>99%, Sinopharm) were milled with 316 stainless milling balls ($\phi 1\text{mm}:\phi 3\text{mm}=3:2$ mass) for 3 h in a planetary ball mill (HLXPM- $\phi 10\text{X4}$, Hengle), with both revolution and rotation speeds of 120 r.p.m. The milled solid salts were blended with nanoparticles (TiB_2 (mean size 50nm, 99%, ChaoWei) and ZrB_2 (mean size 50nm, 99%, ChaoWei)), in a weight ratio of 1:1, followed by ultrasonic dispersion in acetone at 100 kHz for 2 h. Finally, the mixture in a slurry form was dried in a vacuum drying oven at 120 °C for 1 h.

Figure 5 Stepwise schematic of preparation of nanoparticles-containing solid salts.

Electrophoretic deposition process in molten salts. For all the experiments of EPD, the procedures of preparation of high-temperature molten salts containing nanoparticles are as follows. The mixture of NaF and AlF_3 (61:39 mol) or NaCl, KCl and AlCl_3 (>99%, Aladdin) (45:45:10 mol) were introduced to a graphite crucible, which was placed in an electric resistance furnace, heated up to temperatures of 980 °C and 710 °C, respectively. After the mixture was melted, the prepared solid salts containing nanoparticles mentioned in the above section were added to the molten salts, resulting in molten salts including nanoparticles with a required content. The resulting molten mixture stabilized for 10-20 min, followed by the subsequent process.

As shown in Fig. 1a, the high-temperature molten salts including nanoparticles were contained in a crucible. A molybdenum or graphite cathode ($4*1*25$ mm or $8*3*30$ mm), with an immersion depth of 10-20 mm, and a graphite anode with an immersion depth of 15-20 mm were placed in the cell. Before use the cathodes were ground by successively finer SiC sandpaper, followed by an ultrasonic cleaning in acetone and dried for use. In molten fluorides and chlorides, the temperature was controlled at 980 °C and 710 °C, respectively. Pre-electrolysis under 1.5 V cell voltage for 1 h was needed to remove some impurities. The EPD was under a constant voltage mode, ranging from 1.2-1.5 V for 1 h. A DC power supply (HLR-3660D, Henghui) was used to perform the potentiostatic control. All the EPD were performed in an argon atmosphere.

After the EPD was terminated, the coated cathode was removed from the cell. After the coated cathode was withdrawn from the molten chlorides, it was immersed in deionized water for 1h to remove the solid chloride salt residues, in acetone for 5min to remove the water, followed by drying. After the coated cathode was withdrawn from the molten fluorides, it was soaked in molten NaCl-KCl at 710 °C for 5min to remove the solid fluoride salt residues and the subsequent processing was the same as for coated cathodes prepared in molten chlorides.

The coated molybdenum was embedded in epoxy resin at room temperature and ground by successively finer SiC sandpaper, followed by polishing using diamond abrasion paste, resulting in the sample of cross-section of TiB_2 coating (Fig. 1f). The coated graphite was broken down to obtain the fractured cross-section of the TiB_2 and ZrB_2 coatings (Fig. 3b and 4c,d).

Characterization. The EPDed coatings were examined using a SEM (Regulus 8220, HITACHI), TEM (JEM-2100, JEOL) and XRD (Smart Lab, Rigaku) to analyze their micromorphology, microstructure and phase composition. TEM samples were prepared using a precision ion polishing system (Model 691, Gatan) for Fig. 4 e,f.

The EPDed coatings were ground by successively finer SiC sandpaper to obtain a smooth surface for nanoindentation tests. Their hardness and elastic modulus were assessed by a nanoindenter (Nano Indenter G200, Agilent). Six indentations tests on various parts of each coating were conducted to ensure the reliability.

For thick coatings, the surface micro-hardness was measured with a Vickers micro-hardness tester (MH-5LD, Hengyi) using a load of 100 gf.

Figures

Figure 1

a, Schematic of electrophoretic deposition (EPD) in molten salts. b, X-ray diffraction (XRD) pattern of the deposited coating on a molybdenum substrate in TiB_2 nanoparticle-containing molten NaF-AlF_3 (61:39 mol) system under a potentiostatic mode (1.2 V) at a temperature of 980 $^\circ\text{C}$. c-e, Scanning electron

microscopy (SEM) images (c,d) and photograph (e) (polished) (note the reflection of the pencil) of TiB₂ coating. f, Micrographs of the cross-section of TiB₂ coating. g, The dependence of indentation hardness and elastic modulus on the indentation depth for the TiB₂ coating.

Figure 2

Micromorphology of quenched sample of TiB₂ nanoparticle-containing melt located in the upper part of molten fluorides with the addition of TiB₂ nanoparticles 5 h before.

Figure 3

a, SEM image and photograph (top-left inset) of the EPDed coating on a graphite substrate in TiB₂ nanoparticle-containing molten NaF-AlF₃ (61:39 mol) system under potentiostatic mode (1.2 V) for 1 h at

a temperature of 980 °C. b,c, Micrograph of the cross-section (b) and XRD pattern (c) of the TiB₂ coating.

Figure 4

a, SEM images and photograph (top-left inset) of deposited coating on a graphite substrate under a potentiostatic mode (1.5 V) in molten NaCl-KCl-AlCl₃ (45:45:10 mol) system at a temperature of 710 °C. b-d, XRD pattern (b) and micrographs of the fractured cross-section (c,d) of ZrB₂ coating. e, Typical transmission electron microscopy (TEM) image and its selected area electron diffraction (SAED) pattern (top-right inset) of ZrB₂ coating. f, Lattice-resolved high resolution TEM (HRTEM) image.

Figure 5

Stepwise schematic of preparation of nanoparticles-containing solid salts.